UDC 666.762.93

CERAMICS BASED ON ALUMINUM NITRIDE

M. D. Chernetskaya[1] and I. G. Kuznetsova[1]

Translated from Steklo i Keramika, No. 10, pp. 29 – 30, October, 2003.

The results of studying the effect of Y_2O_3 and CaO additives introduced into ceramic mixtures in the form of oxides and salts on sintering and properties of AlN-based ceramics are discussed. The effect of high-temperature annealing of ceramics in a mixture of nitrogen and hydrogen on its properties is specified.

The problem of producing highly heat-conducting materials remains topical in view of the fast evolution of semiconductors used in household and industrial devices with high power consumption, a high degree of integration and module structure, high reliability and performance rate.

Materials that can be used for these purposes are diamond, cubic boron nitride BN, silicon carbide SiC, beryllium oxide BeO, and aluminum nitride AlN. However, synthesis of diamond and cubic boron nitride is a complicated and costly process. Silicon carbide is a semiconductor with poor high-frequency characteristics, beryllium oxide is toxic. Ceramics based on AlN has an almost perfect combination of properties.

Numerous publications [1] discuss synthesis of AlN powders, the effect of additives and firing procedures on sintering and properties of ceramics.

Of all various methods for producing AlN powder, the simplest is the method of simultaneous reduction and nitration of aluminum oxide (Serpek reaction) [1] known as the method of carbothermic synthesis carried out at relatively low temperatures (1500 – 1700°C). Using this method, the Redkinskii Experimental Works produces AlN powder of increased purity for ceramics with high thermal conductivity (TU6-00-1014813-215–88 and TU6-00-05808009-268–93). The technology for production of this powder has been developed at the Department of Chemical Technology of Ceramics and Refractories at D. I. Mendeleev Russian Chemical Engineering University together with the Redkinskii Experimental Works (RF Patent No. 1828637).

Since aluminum nitride is a covalent compound, its sintering is related to certain difficulties: dispersion of powder should be very high (particle size not more than 0.5 μm) and the firing temperature should be 1900 – 1950°C.

It is possible to produce dense ceramics at lower firing temperatures using initial powders with lower dispersion, if sintering takes place according to the liquid-phase mechanism of dissolution-crystallization. To develop conditions for liquid phase formation, oxide additives are introduced, which react with the main material and facilitate its sintering and growth of AlN crystals.

The effect of an activating additive on sintering depends not only on the type of additive, which determines the composition of the liquid phase, but on the uniformity of its distribution, especially when small quantities are introduced. A small quantity of additive has to be uniformly distributed for the emerging liquid phase to moisten all AlN particles.

In the present study we investigated the effect of Y_2O_3 and CaO additives introduced into mixture in the form of oxides and salts on sintering of AlN and properties of ceramics,

The studies were carried out on powder synthesized by the carbothermic method at a temperature of 1550°C, which in its granulometric composition constitutes loose aggregates of white or light gray color, sized from 10 to 20 μm, the size of grains in the aggregates ranging from below 1 to 2 μm. The content of nitrogen is 32.5% (here and elsewhere mass content, unless otherwise specified).

The following compounds were introduced as activating additives in amounts from 0.25 to 2.0% (above 100% of the main AlN converted to respective oxide): Y_2O_3 (grade ITO-2), Y_2O_3 obtained by calcination of $Y_2(C_2O_4)_3$; $Y(NO_3)_3 \cdot 6H_2O$; $CaCO_3$; $Ca(NO_3)_2 \cdot 4H_2O$.

The introduction and distribution of the activating additive in the form of dry salt and finely disperse powder Y_2O_3 was implemented by mixing in the course of milling.

The introduction of activating additives via solutions of yttrium and calcium salts was implemented in the form of nitrates $Y(NO_3)_3 \cdot 6H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ in an anhydrous solvent (acetone). The dissolved additive was introduced into milled AlN powder

To obtain ceramics, samples molded by semidry molding were fired at a temperature of 1750 – 1850°C in a nitrogen flow.

[1] D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

TABLE 1

Parameter	Ceramics based on AlN	
	before annealing	after annealing
Apparent density, g/cm^3	3.25 – 3.27	3.25 – 3.28
Open porosity %	0.0 – 0.3	0.0 – 0.1
Bending strength, MPa	250 – 350	200 – 250
Thermal conductivity, W/(m · K)	70 – 140	150 – 180
Dielectric loss tangent, 10^{-4}, at frequency:		
10^6 Hz	1 – 8	1 – 4
10^{10} Hz	20 – 30	15 – 20
Dielectric permeability	7.8 – 8.5	7.9 – 8.3
Specific volume resistivity at temperature 25°C, Ω · cm	10^{12}	10^{13} – 10^{14}

The data characterizing sintering of materials (Fig. 1) indicate that it is advisable to introduce a small quantity of activating additive in the form of respective salt compounds via a solution to obtain uniformly sintered articles. In this case a uniform distribution of additive in the powder volume is accomplished already at the stage of mixing the initial batch. In studying the effect of yttrium and calcium salts on AlN sintering, no fundamental difference was registered, which is due to similarity of the processes in decomposition of these salts in sintering.

A decrease in the density of ceramics when a great quantity of additive $Ca(NO_3)_2 \cdot 4H_2O$ is used, is due to the formation of sealed porosity caused by evaporation of emerging calcium aluminates. The presence of intercrystalline porosity is corroborated by petrography analysis data.

It can be seen from Fig. 1 that introducing 2% yttrium oxide additive it was possible to sinter ceramics to a dense state (99% of the theoretic value) at 1750°C with a 4-h exposure at the maximum temperature. The open porosity in this case was below 0.1%.

It is advisable to introduce a decreased quantity of activating additive via a salt solution, upon which ceramics with relative density 98% was obtained already with 0.5% additive.

To form a vacuum-dense structure in ceramics, it is preferable to use Y_2O_3 additive obtained by calcination of $Y_2(C_2O_4)_3$. In this case open porosity below 0.3% was reached introducing 0.5% additive.

Although ceramics with calcium and yttrium oxide additives introduced by various methods had high density, its thermal conductivity was low (70 – 140 W/(m · K)) owing to the presence of the second phase (yttrium and calcium aluminates).

A high level of thermal conductivity was obtained after high-temperature annealing of ceramics with 2% Y_2O_3 additive at 1850°C and a 4-h exposure in a flow of mixed nitrogen and hydrogen gases (hydrogen content 10 – 15 vol.%). In annealing the size of AlN crystals increases, the content of the second phases and microimpurities decreases (RF patent No. 2029752). This is responsible for an increase in thermal conductivity of AlN-based ceramics to 150 – 180 W/(m · K) after annealing, an increase in resistivity to 10^{13} – 10^{14} Ω · cm and a decreased dielectric loss tangent (Table 1).

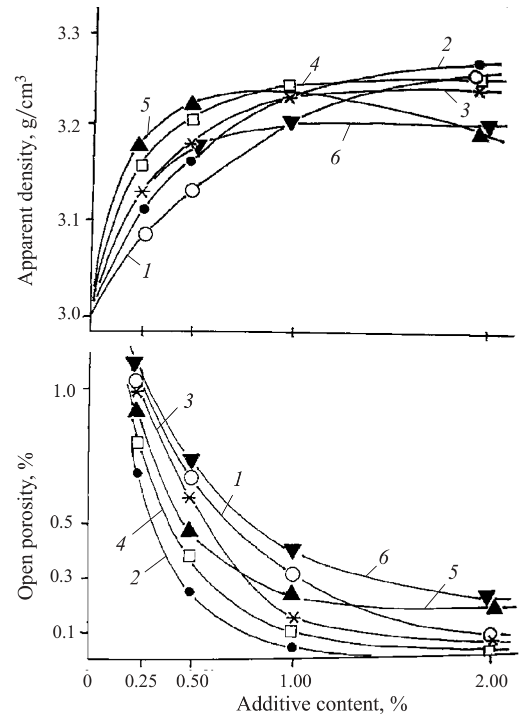

Fig. 1. The effect of the type, quantity and method of introducing the sinter-activating additive on apparent density and open porosity of ceramics based on AlN (firing temperature 1750°C, exposure 4 h): *1*) Y_2O_3 (ITO-2); *2*) Y_2O_3 obtained by calcination of $Y_2(C_2O_4)_3$; *3*) $Y_2(C_2O_4)_3$; *4*) $Y(NO_3)_3 \cdot 6H_2O$; *5*) $Ca(NO_3)_2 \cdot 4H_2O$; *6*) $CaCO_3$.

Thus, sinter-activating additives Y_2O_3 and CaO have an effect on sintering, microstructure, and properties of AlN-based ceramics.

Introduction of Y_2O_3 and CaO as salt solutions makes it possible to decrease to 0.5% the quantity of additive required to obtain high-density materials.

High-temperature annealing of ceramics based on AlN with 2% Y_2O_3 additive in a gas medium of mixed nitrogen and hydrogen raises is thermal conductivity and improves its electrophysical properties.

REFERENCES

1. G. V. Samsonov, *Nonmetallic Nitride* [in Russian], Naukova Dumka, Kiev (1969).